

Contents lists available at [SciVerse ScienceDirect](http://SciVerse.ScienceDirect.com)

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Effect of powdered activated carbon technology on short-cut nitrogen removal for coal gasification wastewater

Qian Zhao, Hongjun Han^{*}, Chunyan Xu, Haifeng Zhuang, Fang Fang, Linghan Zhang

State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- The PACT and SBNR combined system enhanced the TN removal efficiency for CGW.
- The SBNR performance was positively related with PACT removal efficiency.
- The PAC removed some recalcitrant compounds, which was indispensable for SBNR.

ARTICLE INFO

Article history:

Received 7 March 2013

Received in revised form 13 April 2013

Accepted 14 April 2013

Available online 22 April 2013

Keywords:

Coal gasification wastewater

Powdered activated carbon

Short-cut nitrogen removal

Biodegradability

Chromaticity

ABSTRACT

A combined process consisting of a powdered activated carbon technology (PACT) and short-cut biological nitrogen removal reactor (SBNR) was developed to enhance the removal efficiency of the total nitrogen (TN) from the effluent of an upflow anaerobic sludge bed (UASB) reactor, which was used to treat coal gasification wastewater (CGW). The SBNR performance was improved with the increasing of COD and TP removal efficiency via PACT. The average removal efficiencies of COD and TP in PACT were respectively 85.80% and 90.30%. Meanwhile, the $\text{NH}_3\text{-N}$ to $\text{NO}_2\text{-N}$ conversion rate was achieved 86.89% in SBNR and the total nitrogen (TN) removal efficiency was 75.54%. In contrast, the AOB in SBNR was significantly inhibited without PACT or with poor performance of PACT in advance, which rendered the removal of TN. Furthermore, PAC was demonstrated to remove some refractory compounds, which therefore improved the biodegradability of the coal gasification wastewater.

© 2013 The Authors. Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

1. Introduction

Discharge of coal gasification wastewater (CGW) wastewater would cause significant deterioration of the environment due to the presence of nutrients especially hazardous substances and persistent compounds, for its high strength in refractory organics and ammonia (Gai et al., 2008; Wang et al., 2011a,b). CGW treatment is the most difficult pollution control task in the coal chemical industry. Regardless of economic value, ozonation, wet air oxidation (Freese and Rolinski, 1984), Fenton-coagulation (Liu et al., 2004) had been effectively used to remove organic compounds, in terms of BOD_5 , $\text{NH}_3\text{-N}$, volatile phenol and chroma. In contrast, activated sludge system was cost-effective over the physiochemical methods for less energy or chemicals required.

According to the reports, two-stage anaerobic reactor has been successfully applied as first step in the full-scale treatment plant (Wang et al., 2011a). With it, COD and total phenol could be remarkably removed, especially after employed optimal feeding mode and proper co-substrate (Wang et al., 2010, 2011b). But the ammonia nitrogen, as well as the remaining COD, phenol, other pollutants which exhibit poor removal efficiency in anaerobic process needed to be removed by the followed aerobic treatment in order to meet the requirement of concerned standard. However, the conventional activated sludge may not so effective to accomplish the biological nitrogen removal of CGW. Li et al. (2011) found that nitrification in MBBR would be easily inhibited especially during the start-up period or sudden increasing of COD or $\text{NH}_3\text{-N}$ in the CGW influent. Similarly, Ramos et al. (2007) used submerged fixed-film reactor to accomplish biological nitrogen and phenol removal from saline industrial wastewater and found that this process was not able to achieve a nitrogen oxidation superior to 63%, in spite of a sufficient supply of oxygen and the diluting effect of high recirculation (600%) on the phenol concentration in the influent. One reason for the low efficiency of total nitrogen removal was attributed to the harmfulness and toxicity of CGW. Typical nitrification inhibitors, such as phenol, polynuclear aromatic hydrocarbons, and nitrogen heterocyc-

^{*} Corresponding author. Address: School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090 China. Tel.: +86 451 87649777; fax: +86 451 86283082.

E-mail address: han13946003379@163.com (H. Han).

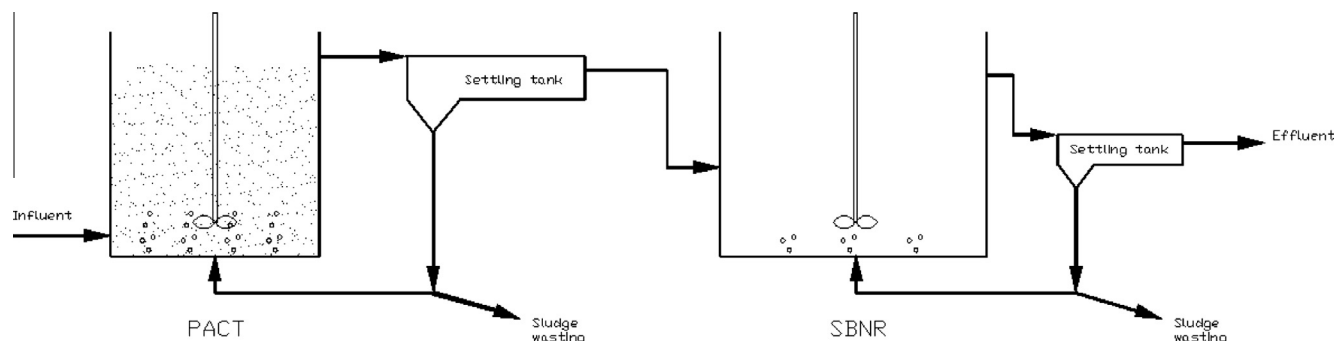


Fig. 1. Schematic diagram of the pilot-scale combined PACT and SBNR process.

clic compounds resulted in insufficient nitrification. Another explanation could be inadequate carbon resource for denitrification. The COD/N value was only an apparent overall indicator; the stoichiometric parameter is in fact the denitrification potential of wastewater, i.e. the fraction of organic carbon available for denitrification (Hocaoglu et al., 2011). Therefore, due to the distinct characteristic of CGW, problems of toxicity and carbon source need to be solved so as to achieve high total nitrogen removal rate.

To reduce the negative impact of toxicity of PAH, activated sludge coupling with activated carbon adsorption, i.e. powdered activated carbon technology (PACT) was a promising method to remove aromatic compounds (Quan et al., 2005), such as phenol (Sundstrom et al., 1979; Cansado et al., 2012), 3,5-dichlorophenol (Widjaja et al., 2004), 2-chlorophenol (Aktas and Cecen, 2007). Particularly, it is also a cost-effective method due to its bioregenerability by the biomass bulk. Due to the low BOD₅/N ratio of CGW, shortcut nitrification process seems feasible method, owing to less carbon resource demand as well as less oxygen demand. In the shortcut biological nitrogen removal (SBNR) process, ammonia is partially oxidized to nitrite and the nitrite is directly reduced to dinitrogen (N₂). It uses a shortcut microbial pathway instead of the complete oxidation via NO₃-N in the overall reaction (Hwang et al., 2006). The process can be obtained through appropriate manipulation of pH, SRT, DO, free ammonia (FA) concentration (Yang et al., 2007). Besides, the NH₃-N in CGW was in the range of approx. 100–200 mg/L, which ensured a successful start-up of short-cut biological nitrogen removal reactor (Park et al., 2010).

However, in previous studies of CGW wastewater treatment, work on improvement of total nitrogen removal was rare. No work on both eliminating toxicity and enhancement of denitrification via short-cut has been done in CGW wastewater treatment. So in the current study, performance of PACT coupling with SBNR was discussed. Moreover, the role of PACT in the TN removal was investigated. The process was tested to be feasible and preferable reference to further engineering application.

2. Methods

2.1. Experimental setup

Two quadrate aeration containers (shown in Fig. 1), one acted as PACT and the other one as SBNR reactor, were constructed of cubic plexiglass. The quadrate aeration tank with a working volume of 3.8 L was made of 16 cm in length, 16 cm in width, 15 cm in height. The horizontal flow sedimentation tank after PACT was of a total working volume of 0.7 L. The sludge from the sedimentation was pumped back to the PACT reactor. The SBNR dimensions were: 30 cm long, 15 cm wide and 15 cm high, with a total working volume of 5.7 L. The spacing baffle was placed in the SBNR, which was separated into two parts: the aerobic compartment and anoxic compartment, with volume ratio of 2:1. The horizontal flow

sedimentation tank after PACT was of a total working volume of 0.5 L. The reactors were operated at room temperatures of 28 ± 5 °C in summer (Yang et al., 2007; Wu et al., 2009), while in winter time, the SBNR were maintained at 32 ± 1 °C by electrothermal thread warming system.

2.2. Characteristic of sludge and wastewater

Seed sludge for PACT and SBNR was respectively obtained from the full-scale aerobic tank 1 (after anaerobic process) and aerobic tank 2 (after aerobic tank 1) treating Lurgi coal gasification wastewater at China Coal Longhua Harbin Coal Chemical Industry Co., Ltd. The plant had been operating over 2 years. The average temperature of the raw wastewater in 1 year was around 35 °C. The sludge was grey-black with good settlement property. The PACT and SBNR tank were inoculated with around 20 and 15 g of volatile suspended. The VSS/SS ratio of the seed sludge was about 0.7.

The raw wastewater employed in the current study was synthesized according to the effluent composition of anaerobic reactors in the Lurgi gasification wastewater treatment plant (Coal Longhua Harbin Coal Chemical Industry Co., Ltd, China). The concentration of COD, BOD₅, NH₃-N, total phenols, volatile phenols in the real wastewater were 1350, 401, 154, 420 and 102 mg/L, respectively. NH₃-N in the anaerobic outlet was slightly higher than that in the inlet (data not shown), indicating there was no NH₃-N reduction but increase instead. And the BOD₅/COD was approx. 0.30. The PACT tank was fed with the synthetic wastewater 1 (SW1) consisted of crude phenol obtained from the same company, phenol, sodium acetate, NH₄Cl of analysis grade, and the following macro-nutrients: 50 mg/L MgSO₄·7H₂O, 20 mg/L K₂HPO₄, 20 mg/L CaCl₂·2H₂O, 15 mg/L FeSO₄·7H₂O, 10 mg/L KH₂PO₄, 15 mM/L NaHCO₃. The main characteristic of SW1 was shown in Table 1.

During the start-up, the SBNR was fed with synthetic wastewater 2 (SW2), with phenol of 432 mg/L, NH₄Cl of 550 mg/L (144 mg NH₃-N/L) and NaHCO₃ of 1728 mg/L (20.60 mM/L).

2.3. Start-up and operation

The two reactors were started separately. In the beginning, PACT tank was fed with raw wastewater. Gradually, the synthetic waster was added into the feed with ratio increasing to allow the biomass to acclimatize with SW1. With SRT controlled at 12–15 d, much NOB in the seed sludge could be washed and AOB and NO₂ concentration started accumulated in the aerobic compartment of SBNR. Then steady-state operation lasted for months. 20 d and 15 d of SRT were used for PACT and SBNR respectively. When PACT was running stably and successfully, the followed SBNR was fed with PACT outlet. During this period, sodium acetate of 50 g/L as additional carbon resource was pumped into the SBNR anoxic compartment with flow rate of 0.01 L/h.

Table 1
Main characteristics of raw wastewater.

Parameters	Value
COD (mg/L)	1207.4–1530.9
BOD ₅ (mg/L)	327.1–394.7
TOC (mg/L)	406.8–569.3
NH ₃ -N (mg/L)	149.6–159.3
Volatile phenols (mg/L)	459.2–608.0
Bicarbonate alkalinity (mmol/L)	10–15
pH	7.2–7.3

Table 2
PACT operating condition.

Condition	Inlet	PACT operation condition
1	SW2	Without PACT
2	SW1	Without PACT
3	Effluent of PACT	PAC dosage = 0.2 g/L, HRT = 12 h, DO = 0.5 mg/L
4	Effluent of PACT	PAC dosage = 0.5 g/L, HRT = 12 h, DO = 2 mg/L
5	Effluent of PACT	PAC dosage = 1 g/L, HRT = 24 h, DO = 4 mg/L

2.4. Effect of PACT performance on total nitrogen removal in the SBNR

In order to investigate the relationship between PACT and SBNR, nitrite accumulation and TN removal efficiency by SBNR was compared in different scenarios- with PACT under different operating conditions, i.e. with different HRT, DO and powdered activated carbon (PAC) dosage (shown in Table 2). Each lasted more than 20 days.

2.5. Enhancement of biodegradability by PACT

The biodegradability test was conducted to study the role of PAC in nitrogen removal. SW1 and PACT outlet under condition 5 was directly used as test objects and SW1 after 12 h adsorption by 1 g/L PAC at DO of 4 mg/L, i.e. the supernatant after adsorption by activated carbon (SAAC) was selected as control. Gas chromatography-mass spectrometry (GC-MS) was assayed for the three samples above to valuate the PAC adsorptive preference. Thereafter, FTIR test was used to highlight and validate the GC-MS analysis.

2.6. Fish

Sludge from PACT and SBNR were fixed in 4% paraformaldehyde solution from 8 h at 4 °C on day 30. After dispersed by ultrasonic treatment for 1 min, 5 µl of the sample was placed on a slide coated with 0.1% gelatin and dried overnight. Then the specimen was immersed and dehydrated by successive 50%, 80%, and 99.5% ethanol solution (3 min each) and air dried. Then after 90 µl hybridization buffer (0.9 mol/L NaCl, 20 Mmol/L Tris-hydrochloride (pH 7.2) 0.01% sodium dodecyl sulfate, and formamide) and 10 µl probe, the in situ hybridizations were performed in a hybridization incubator at 46 °C for 3 h. FISH probes used in the experiments were NSO190 with fluorescence tag FITC (for ammonia oxidizing β-Proteobacteria) and Ntspa662 (for Nitrospira) with fluorescence tag TRITC. In the hybridization buffer, formamide concentration for NSO190 and Ntspa662 were 55% and 35%, respectively. Hybridization was followed by a thorough washing step, which was carried out twice, at 48 °C for 20 min with 50 ml of pre-warmed washing Buffer. The slides were mounted with to avoid bleaching and examined with an OLYMPUSBX52 fluorescence microscope.

2.7. Analytical methods

COD, BOD₅, SS, VSS, total phenols (TP), oil, ammonia NH₃-N and NO₂-N were measured according to Standard Methods (APHA, 1998). The COD concentrations and TP in the PACT and NH₃-N, NO₂-N in the SBNR were analyzed once daily. The NO₃-N and TN was analyzed once every 2 days. It was worth to note that for BOD₅ analysis, the sludge in the SBNR was used as the inoculum added into the diluted water. Bicarbonate alkalinity were analyzed twice weekly by the distillation method (Anderson and Yang, 1992). DO and pH values were determined daily with a pH meter (pHS-3C, Leici, China) and a DO meter (HACH 30d). During the GC-MS analysis, the pretreatment of waster sample was described in the previous paper (Wang et al., 2011b). In the FTIR assay, the water was dried in vacuum evaporation box and then assayed with Fourier Infrared Spectrometer (Spectrum One B, Perkin Elmer Inc.).

3. Result and discussion

3.1. SBNR start-up and steady operation

3.1.1. Nitrite accumulation and TN removal

For the SBNR in this study, we used a similar strategy for suspended-growth short-cut biological nitrogen removal reported by Park et al. (2010). The SBNR was started up quickly and then stably operated even increased the NH₃-N concentration in the inlet. After 23 days, the nitrite accumulation rate in the aerobic compartment reached a very high level – 1.09 mg NO₂-N/(gVSS h). The conversion rate of NH₃-N to NO₂-N in the aerobic compartment was very high to 95.15% (shown in Table 3), which indicated an absolute superiority of AOB to NOB. The anoxic compartment exhibited a high TN removal efficiency of 89.78%, especially with phenol as carbon source. The microscopy of the aggregated biomass fraction from the aerobic compartment explained a dominance of coccoid and regularly shaped cells arranged in tight clusters. FISH assay revealed that most of these cells reacted with the probes specific for the beta-proteobacterial AOB, belonged to the genus Nitrosomonas. The probes Ntspa662, which are specific for the Nitrosospira spp, showed very weak signal.

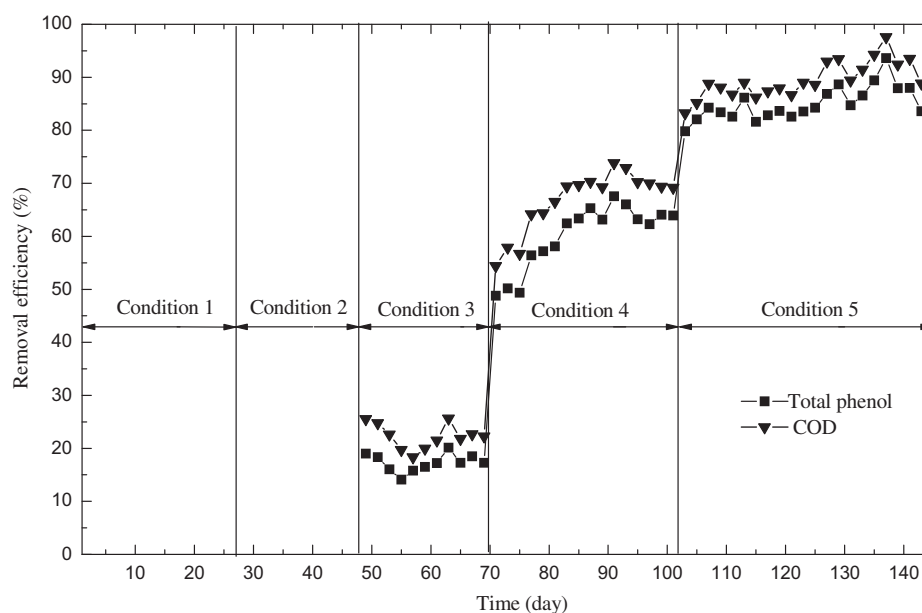
3.2. Influence of PACT performance on SBNR

Figs. 2 and 3 present the relationship between PACT and SBNR performance. As stated above, SBNR achieved high short-cut nitrogen removal efficiency if feeding with SW2. However, when feeding with raw wastewater (condition 2, PACT canceled), the concentration of nitrite decreased dramatically from 137.01 ± 14.15 mg/L to 26.37 ± 4.08 mg/L. The conversion rate of NH₃-N to NO₂-N was only 18.88%, which indicated a severe suppression of AOB activity by the raw water. Thereafter, SBNR was recovered in more than 15 days (data not shown in Fig 2). Converting to condition 3, PACT removed only 17.20% COD and 22.27% of total phenol with 0.2 mg/L PAC dosage, 4 h HRT, 0.5 mg/L DO. Correspondingly, the SBNR was not improved much. The concentration of NH₃-N was still at high level. After further increasing PAC dosage and DO, the PACT achieved higher COD and phenol removal efficiency in condition 4, up to 61.3% and 68%, respectively. Accordingly, the NH₃-N to NO₂-N conversion rate and TN removal rate in SBNR was increased to 60.73% and 48.34%, respectively. Besides, when PACT performance was further improved under optimized condition 5, removal efficiency for COD and phenol were 85.80% and 90.30%, respectively. Thus the less harmful outlet set good foundation for short-cut removal process. And it was reasonable to obtain NH₃-N to NO₂-N conversion rate of 86.89% in SBNR aerobic compartment. Apparently, a sharp increase in NO₃-N also

Table 3

Analysis of N conversion and bicarbonate alkalinity under condition 1–5.

	Condition 1	Condition 2	Condition 3	Condition 4	Condition 5
NH ₃ -N to NO ₂ -N conversion rate (%)	95.15	18.88	36.06	60.73	86.89
TN removal rate (%)	89.78	17.68	24.99	48.34	75.54
Bicarbonate alkalinity (mM/L)	0.50 ± 0.16	1.27 ± 0.16	0.91 ± 0.04	0.42 ± 0.05	0.11 ± 0.07

**Fig. 2.** COD and phenol removal efficiency of PACT under conditions 1–5.

occurred but in fact it did not come from the inlet but produced by nitrite-oxidizing bacteria in PACT. The TIC/TNH (total inorganic carbon: total nitrogen ammonia) of SBNR inlet was 71.76/79.5, i.e. 0.90 and BOD₅/TNH was 335/79.5, i.e. 4.21. At this value, the reduction in conversion rate was in the range concluded by Ganigüé et al. (2012). So compared with condition 1, the slight restrain on AOB might be partly attributed to the CO₂ produced during oxidation of organic matter. It acidified the wastewater and reduced the buffering capacity to balance protons produced (see bicarbonate alkalinity variation in Table 3) during TNH oxidation and eventually reduced NH₃-N conversion rate (Vilar et al., 2010). In the anoxic compartment, the denitrification bacteria can utilize the remaining BOD₅ almost completely, resulting in a TN removal efficiency of 75.54%. Under the optimal Condition 5, PACT exhibited removal percentages of 85.80%, 83.83%, 36.88%, 90.30%, 64.00% for COD, BOD₅, NH₃-N, TP, oil, respectively (shown in Table 4). It was also necessary to note that the chromaticity decreased dramatically after PACT process, which is also in good agreement with Mezohegyi et al. (2012).

It can be concluded that SBNR performance in terms of nitrite accumulation and TN nitrogen removal rate was improved by PACT performance. The operation parameters for PACT, among which PAC dosage was one of the most important (proved by orthogonal experiment, not shown), influenced much on the pollutants removal and therefore influenced much on the nitrogen removal efficiency.

3.3. Biodegradability improvement by PACT

From the above findings, it could be concluded that PACT reactor was indispensable for TN removal of the combined system. And according to the orthogonal test result (not shown), PAC dosage was the most significant among the four important factors. To explore the role of PAC, biodegradability tests compared SW1, outlet

of PACT and SAAC. BOD₅/COD was tested as 0.29 ± 0.01, 0.32 ± 0.02 and 0.34 ± 0.04, respectively. So both the sludge and PAC present in PACT increased the biodegradability. Further analysis can be made based on the organic composition of the 3 streams above (shown in Table 5). The phenol with double or multiple methyl groups and other refractory compounds were partly or completely eliminated by PAC. Specifically, among these compounds, the indole, 6-methyl-4-indanol, *N*-phenyl propanamide, 4,4-dimethyl-*N*-phenyl hexanamide, defined as nitrogen heterocyclic compounds (NHCs) and have been proved to cause great toxicity and harm to the sludge activity, all carried the chromophore, such as -N=, -CO-NH, etc. This fact corresponded with the significant decrease in chromaticity. Thus, the PAC present in the PACT protected the suspended biomass from suffering, while the biomass degraded the remaining phenols, long-chain or aromatic hydrocarbons (Liu et al., 2012), some of which belonged among recalcitrant substances, such as 5,5-dimethyl-2, 4-imidazolidinedione. Sher et al. (2000) found that PACT sludge with high sludge ages was much more resistant to toxic exposure with changes in the biomass rather than sorption on carbon. And the activated sludge also had large and resilient adsorption capacity. It was also revealed that PAC preferentially absorbed aromatic compounds with complex molecule structure rather than simple organic acid, the intermediates produced from the anaerobic metabolism, such as butanoic acid, pentanoic acid, propanoic acid (data not shown). These simple organic acids were quite beneficial for the biomass. Not only were they easily degraded but they might also play a role of co-substrate to promote the degradation of the remaining recalcitrant substances (Bajaj et al., 2008; Ghevariya et al., 2011). Therefore, PACT integrated the advantages from two aspects: adsorption of recalcitrant compounds by activated carbon; adsorption selectivity was also helpful for the sludge to uptake the remaining refractory compounds.

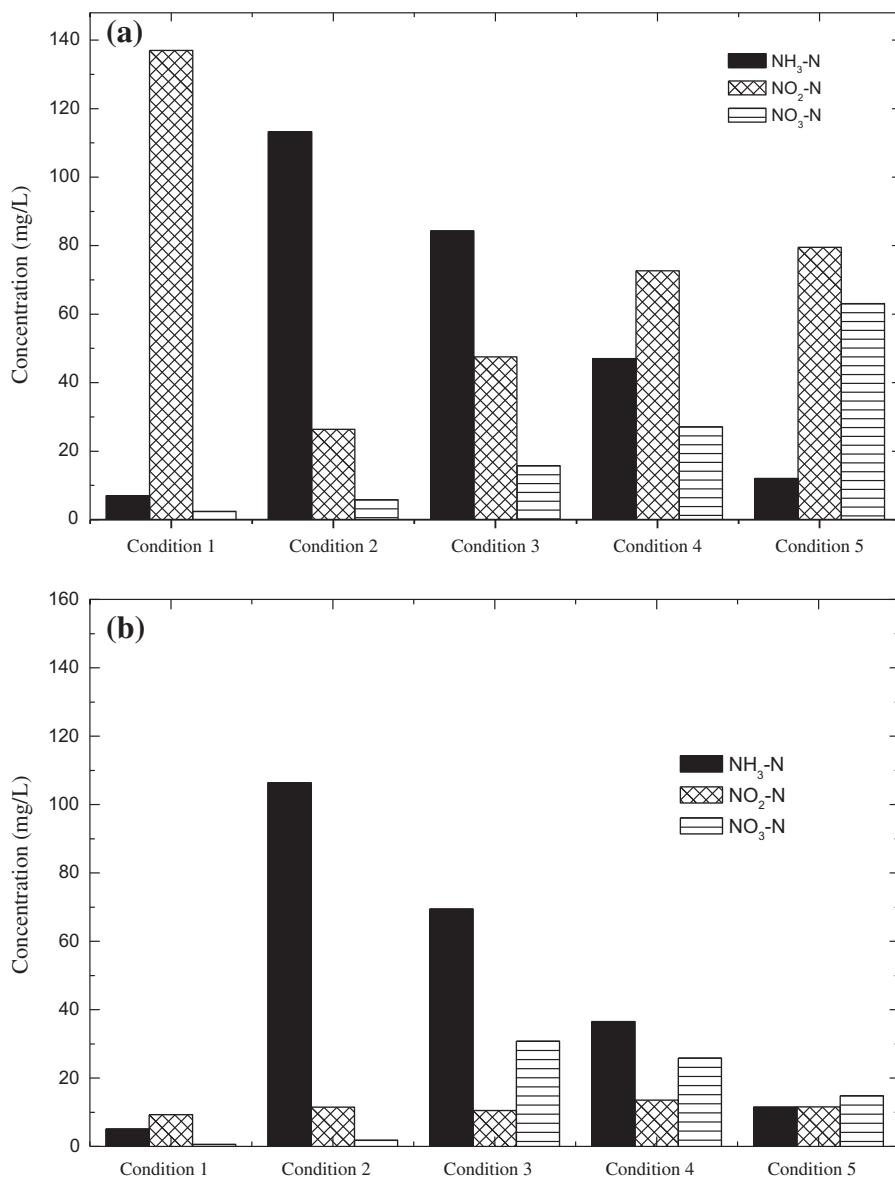


Fig. 3. Contrast in NH₃-N, NO₂-N, NO₃-N concentration of SBNR outlet under condition 1–5. (a) Aerobic compartment and (b) anoxic compartment.

Table 4

Main characteristics of PACT and SNBR outlet under condition 5.

Parameters	PACT		SNBR	
	Mean value \pm standard deviation	Removal rate (%)	Mean value \pm standard deviation	Removal rate (%)
COD (mg/L)	191.63 \pm 37.5	85.80	101.39 \pm 21.05	47.09
BOD ₅ (mg/L)	66.47 \pm 16.2	83.83	15.63 \pm 4.21	76.49
NH ₃ -N (mg/L)	97.20 \pm 5.79	36.88	15.1 \pm 7.09	88.58
NO ₃ -N	60.00 \pm 8.79	–	20.38 \pm 8.41	–
TP (mg/L)	40.75 \pm 11.38	90.30	5.39 \pm 4.59	86.77
Oil (mg/L)	1.8 \pm 1.2	64.00	ND	–
Bicarbonate alkalinity (mmol/l)	2.4 \pm 0.9	–	0.11 \pm 0.07	–
pH	7.2 \pm 0.1	–	7.5 \pm 0.35	–

3.4. Adsorptive preference of PAC for CGW

FTIR spectral analysis allows the identification of different functional groups of the organic substance present in the wastewater. By making a contrast in FTIR spectra of raw wastewater and SAAC, the adsorptive preference of PAC can be concluded. In the FTIR

spectrum, the complex water composition led to many peaks in a wide range of spectrum. As is shown, these two streams had much in common in terms of trends and peaks: The strong peaks near 3400 cm⁻¹ could be due to the hydroxyl group ν (O–H), the ν (C–H) and also ν (N–H) stretches; peaks around 2900–3000 cm⁻¹ indicated the presence of ν (–CH₃); the strong peaks near 1000–1300 cm⁻¹

Table 5

Result of GC–MC analysis for raw wastewater, SAAC and outlet of PACT.

Organic compounds	Raw	A	B	Organic compounds	Raw	A	B
Phenol	28.91 ^a	25.468	4.22	2-Naphthalenol	1.061	ND	ND
Phenol, 2-methyl-	5.486	7.801	2.382	1-Naphthalenol,4-methyl	0.448	ND	ND
Phenol, 3-methyl-	4.537	8.46	ND ^b	Propanamide, N-phenyl-	0.26	ND	ND
Phenol, 4-methyl-	1.404	8.46	3.403	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	ND	ND	7.661
Phenol, 2,4-dimethyl-	1.801	0.336	ND	Dibutyl phthalate	0.19	0.189	ND
Phenol, 3-ethyl-	3.597	2.066	ND	Hexanamide, 4,4-dimethyl-N-phenyl-	0.14	ND	ND
Phenol, 3,5-dimethyl-	3.288	ND	ND	Nonadecane	ND	ND	0.31
Phenol, 2,3-dimethyl-	2.249	0.427	ND	Eicosane	0.16	0.267	0.317
Phenol, 3,4-dimethyl-	3.318	0.511	0.503	Heneicosane	0.349	ND	0.438
Benzene, 1-ethyl-4-methoxy-	3.163	ND	ND	Docosane	0.475	0.178	0.112
Quinoline	1.549	1.032	9.2	Tricosane	0.657	0.455	0.142
Phenol, 2,3,5-trimethyl-	1.156	ND	ND	Tetracosane	0.877	ND	0.793
Indole	0.584	ND	ND	Heptacosane	0.888	0.19	0.901
2,4-Imidazolidinedione, 5,5-dimethyl-	0.733	0.514	ND	1,2-Benzenedicarboxylic acid, diisooctyl ester	0.297	10.643	25.972
Phenol, 2,4,6-trimethyl-	1.978	ND	ND	Hexacosane	0.778	0.307	0.799
dl-5-Ethyl-5-methyl-2,4-imidazolidinedione	1.407	0.657	ND	Hexatriacontane	0.713	ND	ND
6-Methyl-4-indanol	0.484	ND	ND	Nonocosane	0.362	0.245	ND
Others	–	–	–		26.701	31.794	42.847

A, SAAC; B, PACT outlet.

^a Values represent the relative percentage of total peak area.^b ND, not detected.

was typical of $\nu(\text{NH})$ and C–O which could be attributed to the presence of nitrogen groups and phenol, ester or carboxyl groups (COOH). However, these two samples also presented distinction in intensity at some wavelengths. For example, the raw wastewater exhibited an obvious set of peaks emerging in the region of 1600–1700 cm^{-1} , which could be related with $\nu(\text{NO}_2)$, and $\nu(\text{C=O})$ associated with $\nu(\text{CONH-})$ i.e. amino. These were just common chromophoric (Bansal and Sud, 2012) and auxochrome group. In the lower region of the spectra, the raw wastewater showed the more intense absorption bands near 680–880 cm^{-1} , which could be out-of-plane O–H bending attributed to the presence of substituted aromatic. In contrast, these bands are less noticeable on the FTIR spectra of SAAC which contains less aromatic hydrocarbons. Therefore, agreeing with GCMS result, FTIR spectra indicated that PAC adsorbed some organic compounds, leading to a decrease in chromaticity observed.

4. Conclusions

The following conclusion can be drawn from this study:

The developed PACT and SBNR combined process was investigated to enhance the total nitrogen (TN) removal efficiency for the UASB effluent treating CGW. The SBNR performance was highly and positively related with PACT removal efficiency. The PAC partly or completely removed recalcitrant nitrogen heterocyclic compounds (NHCs), thus allowing SBNR to be loaded with a relatively harmless and higher BOD₅/COD influent. The study demonstrated the PACT system could serve as a technically feasible method as a pretreatment for short-cut nitrogen removal for coal gasification wastewater.

Acknowledgements

This work was supported by Sino-Dutch Research Program (SDRP: 2012–2016) and the independent subject sponsored by State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. 2010DX05).

References

- Anderson, G.K., Yang, G., 1992. Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration. *Water Environ. Res.* 64, 53–59.

- Aktas, O., Cecen, F., 2007. Adsorption, desorption and bioregeneration in the treatment of 2-chlorophenol with activated carbon. *J. Hazard. Mater.* 141, 769–777.
- APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.
- Bajaj, M., Gallert, C., Winter, J., 2008. Biodegradation of high phenol containing synthetic wastewater by an aerobic fixed bed reactor. *Bioresour. Technol.* 99, 8376–8381.
- Bansal, P., Sud, D., 2012. Photodegradation of commercial dye, CI Reactive Blue 160 using ZnO nanopowder: degradation pathway and identification of intermediates by GC/MS. *Sep. Purif. Technol.* 85, 112–119.
- Cansado, I.P.P., Mourão, P.A.M., Falcão, A.I., Ribeiro, M.M.L., Carrott, P.J.M., 2012. The influence of the activated carbon post-treatment on the phenolic compounds removal. *Fuel Process. Technol.* 103, 64–70.
- Freese, R.A., Rolinski, E.J., 1984. Wet air oxidation studies of coal gasification wastewaters. *J. Hazard. Mater.* 8, 367–375.
- Gai, H.J., Jiang, Y.B., Qian, Y., Kraslawski, A., 2008. Conceptual design and retrofitting of the coal-gasification wastewater treatment process. *Chem. Eng. J.* 138, 84–94.
- Ganigué, R., Volcke, E.I.P., Puig, S., Balaguer, M.D., Colprima, J., 2012. Impact of influent characteristics on a partial nitrification SBR treating high nitrogen loaded wastewater. *Bioresour. Technol.* 111, 62–69.
- Ghevariya, C.M., Bhatt, J.K., Dave, B.P., 2011. Enhanced chrysene degradation by tolerant *Achromobacter xylosoxidans* using response surface methodology. *Bioresour. Technol.* 102, 9668–9674.
- Hocaglu, S.M., Insel, G., Cokgor, E.U., 2011. Effect of low dissolved oxygen on simultaneous nitrification and denitrification in a membrane bioreactor treating black water. *Bioresour. Technol.* 102, 4333–4340.
- Hwang, S., Jang, K., Jang, H., Song, J., Bae, W., 2006. Factors affecting nitrous oxide production: a comparison of biological nitrogen removal processes with partial and complete nitrification. *Biodegradation* 17, 19–29.
- Li, H.Q., Han, H.J., Du, M.A., Wang, W., 2011. Inhibition and recovery of nitrification in treating real coal gasification wastewater with moving bed biofilm reactor. *J. Environ. Sci.* 23, 568–574.
- Liu, H., Zhou, Z.H., Wu, K.M., 2004. Experimental study of fenton plus coagulation for treating coke effluent. *Environ. Sci. Technol. (China)* 29, 24–27.
- Liu, H.B., Zhao, F., Mao, B.Y., Wen, X.H., 2012. Enhanced nitrogen removal in a wastewater treatment process characterized by carbon source manipulation with biological adsorption and sludge hydrolysis. *Bioresour. Technol.* 114, 62–68.
- Mezohegyi, G., Van der Zee, F.P., Font, J., Fortuny, A., Fabregat, A., 2012. Towards advanced aqueous dye removal processes: a short review on the versatile role of activated carbon. *J. Environ. Manage.* 102, 148–164.
- Park, S.J., Bae, W.K., Rittmann, B.E., Kim, S.J., Chung, J.W., 2010. Operation of suspended-growth shortcut biological nitrogen removal (SSBNR) based on the minimum/maximum substrate concentration. *Water Res.* 44, 1419–1428.
- Quan, X.C., Yang, Z.F., Shi, H.C., 2005. The effect of a secondary chlorophenol presence on the removal of 2,4-dichlorophenol (2,4-DCP) in an activated sludge system bioaugmented with 2,4-DCP degrading special culture. *Process Biochem.* 40, 3462–3467.
- Ramos, A.F., Gómez, M.A., Hontoria, E., González-López, J., 2007. Biological nitrogen and phenol removal from saline industrial wastewater by submerged fixed-film reactor. *J. Hazard. Mater.* 142, 175–183.
- Sher, M.I., Arbuckle, W.B., Shen, Z.Y., 2000. Oxygen uptake rate inhibition with PACT sludge. *J. Hazard. Mater.* B73, 129–142.

- Sundstrom, D.W., Klei, H.E., Tsui, T., Nayar, S., 1979. Response of biological reactors to the addition of powdered activated carbon. *Water Res.* 13, 1225–1231.
- Vilar, A., Eiroa, M., Kennes, C., Veiga, M.C., 2010. The SBNR process in the treatment of landfill leachate. *Water Sci. Technol.* 61, 47–52.
- Wang, W., Ma, W.C., Han, H.J., Li, H.Q., Yuan, M., 2011a. Thermophilic anaerobic digestion of Lurgi CGW in a UASB reactor. *Bioresour. Technol.* 102, 2441–2447.
- Wang, W., Han, H.J., Yuan, M., Li, H.Q., Fang, F., Wang, K., 2011b. Treatment of coal gasification wastewater by a two-continuous UASB system with step-feed for COD and phenols removal. *Bioresour. Technol.* 120, 5454–5460.
- Wang, W., Han, H.J., Yuan, M., Li, H.Q., 2010. Enhanced anaerobic biodegradability of real coal gasification wastewater with methanol addition. *J. Environ. Sci.* 22, 1868–1874.
- Widjaja, T., Miyata, T., Nakano, Y., Nishijima, W., Okada, M., 2004. Adsorption capacity of powdered activated carbon for 3, 5-dichlorophenol in activated sludge. *Chemosphere* 57, 1219–1224.
- Wu, L.N., Peng, C.Y., Zhang, S.J., Peng, Y.Z., 2009. Nitrogen removal via nitrite from municipal landfill leachate. *J. Environ. Sci.* 21, 1480–1485.
- Yang, Q., Peng, Y.Z., Liu, X.H., Zeng, W., Takashi, M., Hiroyasu, S., 2007. Nitrogen removal via nitrite from municipal wastewater at low temperatures using real-time control to optimize nitrifying communities. *Environ. Sci. Technol.* 41, 8159–8164.